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(21) International Application Number: PCT/US95/11052 (22) International Filing Date: 13 September 1995 (13.09.95) (30) Priority Data: 94202736.8 22 September 1994 (22.09.94) EP (34) Countries for which the regional or international application was filed: NL et al. (71) Applicant (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): GARCIA DURAN, Juan-Antonio [ES/CH]; 26, avenue de l'Amandolier, CH-1208 Geneva (CH). ROLLAND, Loïc, Pierre [FR/FR]; Résidence Metna, 234, avenue de Grande-Champagne, F-01220 Divonne-les-Bains (FR). (74) Agents: EVANS, Craig, H. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: CA, JP, NO, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: FLEXIBLE NONHALOGEN-CONTAINING THERMOPLASTIC POLYOLEFIN COMPOSITIONS		
(57) Abstract Nonhalogen-Containing Thermoplastic Polyolefin blends are provided which are flexible and are particularly useful in replacing polyvinyl chloride sheeting used as roofing liners. The blends comprise, in general, (1) ethylene vinyl acetate, (2) very low density polyethylene, (3) ethylene vinyl acetate carbon monoxide terpolymer and optionally contains (4) a compatibilizer blend comprising (i) a polar olefinic polymer and (ii) a non-polar olefinic polymer; all of which are chlorine free.		

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Title

Flexible Nonhalogen-Containing Thermoplastic Polyolefin Compositions

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Background of the Invention

10 Field of Invention:

This invention relates to polyolefin compositions and more particularly to such compositions which are flexible and to shaped articles made from them.

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Background Discussion:

Polyvinyl chloride (PVC) sheets have been on the market for many years and have become the standard roof liner material in the housing industry. PVC sheets are characterized as being flexible over a variable temperature range, heat-sealable, and oil-resistant. However, with the trend toward a chlorine-free environment, there is a need for a PVC sheeting alternative. Ethylene-propylene-diamine-methylene (EPDM) rubbers are alternatives, but these are difficult to seal. Thus, there is a need for roof and other types of liner sheets which are thermoplastic and heat-sealable, halogen-free and flexible.

WO 93/19118 and WO 89/06256 disclose PVC-free compositions that are suitable for use as coatings for electrical cables. These compositions contain several components that are similar to those described, but lack, i.a., the terpolymer described herein.

Summary of the Invention

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According to the present invention there is provided a flexible, nonhalogen-containing polymer composition which comprises a blend of:

- (1) ethylene vinyl acetate containing 30-90% by weight ethylene and 10-70% by weight vinyl acetate,
- 5 (2) very low density polyethylene having a specific gravity less than 0.920, and
- (3) ethylene vinyl acetate carbon monoxide terpolymer containing 30-90% by weight ethylene, 10-70% by weight vinyl acetate
10 and 1-20% by weight carbon monoxide.

The composition according to the invention may further contain:

- (4) a compatibilizer blend comprising
- 15 (i) a polar olefinic polymer containing 15 to 60% by weight ethylene vinyl acetate; and
- (ii) a non-polar olefinic polymer,

wherein one of components (4)(i) and (4)(ii) contains 0.01 to 10%
20 by weight of glycidyl acrylate or methacrylate or a derivative thereof, and the other of components (4)(i) and (4)(ii) contains 0.01 to 10% by weight of a carboxylic acid or a derivative thereof.

Common additives which may be included in the composition of
25 the present invention include aluminium trihydrate (for flame retardancy), antioxidants, titanium dioxide (for UV resistance and to give a white color to the product) and UV stabilizers.

Detailed Description of the Invention

30 The present invention relates to flexible, non-halogen containing thermoplastic polymer blends which are useful in sheet form, and particularly as roofing liners. These blends generally are formed by combining an ethylene vinyl acetate (EVA) copolymer and a
35 very low density polyethylene (VLDPE) having a specific gravity below 0.920, both of which are chlorine free.

The blend may further contain an ethylene vinyl acetate carbon monoxide (EVACO) terpolym r. Compatibilizing agents can be added in order to improve the properties of the blend.

- 5 Polymer blends according to the present invention can be formed into sheets which have many properties comparable to polyvinyl chloride (PVC) containing blends, but with better elongation and being free from chlorine.
- 10 Unless otherwise stated, percentage weight ranges for each of the components in the composition of the present invention are calculated exclusive of any additives which may be present.

- The EVA copolymer (component (1)) useful in this invention
- 15 preferably contains 30-90% by weight of ethylene and 10-70% by weight of vinyl acetate, more preferably 55-75 % by weight of ethylene and 25-45 % by weight of vinyl acetate. In general, these EVA's have a melt flow index (MFI) in the range of 0.05-100 g/10 min., preferably less than 50 g/10min. as determined by ASTM D-
- 20 1238 (measured at 2.16 kg and 190 °C) and are well-known in the art.

- Component (1) preferably comprises 5-65% by weight of the composition of the present invention, more preferably 20-50% by
- 25 weight, still more preferably 20-30% by weight.

- The VLDPE (component (2)) is used herein to mean polyethylene having a density below about 0.920 g/cc and includes linear polyethylene as well as copolymers of ethylene which are
- 30 thermoplastic resins, but non-polar. The term VLDPE includes copolymers of ethylene and other alpha-olefins such as 1-butene, 1-hexene, and 1-octene. The processes for producing VLDPE are well known in the art and commercial grades of this polyolefin are available.

- 35 Component (2) preferably comprises 5-65% by weight of the composition of the present invention, more preferably 10-40% by weight, still more preferably 10-30% by weight.

The EVACO terpolymer (component (3)) useful in this invention preferably contains 30-90% by weight of ethylene, 10-70% by weight of vinyl acetate and 1-20% by weight of carbon monoxide, more preferably 55-65% by weight of ethylene and 20-30% by weight of vinyl acetate and 5-15% by weight carbon monoxide. In general, these EVACO's have a melt flow index (MFI) in the range of 1-50 g/10 min., preferably in the range of 10-40 g/10min. as determined by ASTM D-1238 (measured at 2.16 kg and 190 °C) and are well-known in the art.

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Component (3) preferably comprises 5-65% by weight of the composition of the present invention, more preferably 20-50% by weight, still more preferably 20-30% by weight.

- 15 The compatibilizing polymer (4)(i) in the compatibilizer blend (component (4)) is a relatively polar olefin polymer containing 15-60% by weight vinyl acetate, more preferably 25-40% by weight vinyl acetate, and optionally containing 1-20% by weight of carbon monoxide; compatibilizing polymer (4)(ii) is a substantially non-
- 20 polar olefin polymer containing less than 15% by weight of a copolymerized polar monomer, more preferably containing less than 5% by weight of a copolymerized polar monomer.

- One of components (4)(i) and (4)(ii) will contain 0.01-10% by weight, preferably 0.5-5% by weight, of reactive groups selected from glycidyl acrylate or methacrylate or a derivative thereof, and the other of components (4)(i) and (4)(ii) will contain 0.01-10% by weight, preferably 0.5-5% by weight, of reactive groups selected from a carboxylic acid or a derivative thereof (such as an
- 25 anhydride) .
- 30

- This olefin backbone polymer of components (4)(i) and (4)(ii) can be functionalized by grafting the desired reactive group to the polymer by known processes. The grafting of the polyolefin can be carried out in the melt state, in solution or in suspension as described in the state-of-the-art literature. While the melt viscosity of the modified polyolefin is not restricted, the most effective compatibilization with modified polyolefin is found if the melt index, measured at 2.16 kg and 190°C is between 1 to 50
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g/10 min. Glycidyl methacrylate and maleic anhydride are the preferred functionalizing agents. Such modified polyolefins can be prepared as described, for example, in published European Patent Application Nos. 370,735 and 370,736.

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The compatibilizer blend will contain 20-80% by weight component (4)(i) and 80-20% by weight component (4)(ii), more preferably 25-35% by weight component (4)(i) and 65-75% by weight component (4)(ii).

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When present, component (4) preferably comprises 0.5-10% by weight of the composition of the present invention, more preferably 3-5% by weight.

- 15 In addition to its polymer components, the composition of the present invention can be blended with common additives such as reinforcing and non-reinforcing fillers, flame retardant fillers such as aluminium trihydrate, antioxidants, UV stabilizers, lubricants (e.g., oleamide), antiblocking agents, antistatic agents, waxes,
- 20 coupling agents for fillers, pigments, titanium dioxide, talc and other processing aids known in the polymer compounding art. The pigments and other additives may comprise up to about 50 weight percent of the total composition based on polymer components plus additives (the polymer components being
- 25 present in amounts with respect to each other in the proportions previously specified); preferably pigments and fillers comprise above about 0 to about 30 weight percent of the total composition.

- The blends of the invention can be prepared by mixing the
- 30 polymeric ingredients and optional additives by use of conventional masticating equipment, for example, a rubber mill, Brabender Mixer, Banbury Mixer, Buss-ko kneader, Farrel continuous mixer or twin screw continuous mixer. Mixing times should be sufficient to obtain homogeneous blends. Satisfactory
- 35 mixing times depend upon the types of polymers and upon the type and amount of compatibilizer. Typically, mixing times of about 5 minutes are satisfactory. If the polymer blend is obviously non-homogeneous, additional mixing is required.

The invention can be further understood by the following examples in which parts and percentages are by weight or in parts per hundred rubber (phr) and temperatures are in degrees Celsius.

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Examples 1-4

Legend

- 10 MFI = melt flow index
EVA - ethylene vinyl acetate
VLDPE = very low density polyethylene
MAH = maleic anhydride
EGMA = ethylene glycidyl methacrylate
15 EVACO = ethylene vinyl acetate carbon monoxide

Procedure

- A blend is prepared by melt-compounding the following
20 components in the proportions set forth in Table 1 below.
- EVA₁ (60% ethylene and 40% vinyl acetate) having a MFI (190°/2.16 kg) of 0.8
 - EVA₂ (72% ethylene and 28% vinyl acetate) having a MFI
25 (190°/2.16 kg) of 3.0
 - EVA₃ (66% ethylene and 33% vinyl acetate) having a MFI (190°/2.16 kg) of 18, grafted with 1% MAH
 - VLDPE₁ having a density of 0.911 g/cc and a MFI (190°/2.16 kg) of 2.2
 - 30 - VLDPE₂ having a density of 0.887 g/cc and a MFI (190°/2.16 kg) of 1.5
 - EVACO (62.5% ethylene, 28.5% vinyl acetate and 9% carbon monoxide) having a MFI (190°/2.16 kg) of 35
 - EGMA (1.8 % glycidyl methacrylate having a MFI (280°/2.16 kg) of 5
35
 - titanium dioxide
 - aluminium trihydrate
 - UV stabilizers (blend of 50% by weight TINUVIN 622 LD (an

- antioxidant - phenolic type available under the name IRGANOX 1010 from Ciba

Melt compounding is carried out on a two roll mill with batches from 100 grams at 130-150°C for ca. 5 minutes. The milled product is formed into a testing plaque in a hydraulic press at 130-150°C for 5 minutes. Afterwards stress-strain testing (ASTM D-638) and Shore A hardness (DIN 53505) are carried out. Results are shown in Table 1.

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Table 1

<u>Example numbers</u>		<u>1</u>	<u>2</u>	<u>3</u>
15	EVA ₁	-	-	5.0
	EVA ₂	22.6	25.2	14.2
	EVACO	25.0	25.0	23.0
	VLDPE ₁	5.0	11.2	-
	VLDPE ₂	13.6	16.5	10.0
20	EGMA	1.0	-	4.0
	EVA ₃ + 1% MAH	1.9	-	4.0
	Titanium dioxide	5.0	1.0	5.0
	Aluminium trihydrate	20.0	20.0	30.0
	UV stabilizer	0.4	0.6	0.4
25	Antioxidant	0.5	0.5	0.4
	Zinc stearate	5.0	-	4.0
	Tensile strength (MPa)	12.0	13.5	13.5
	Tensile elongation (%)	740	750	700
	Shore A hardness	78	80	80
30	Specific gravity (g/cc)	1.150	1.094	1.180

One can see that the formulations containing compatibilizers show a particularly lower hardness and specific gravity. For roofing membranes, this brings a significant benefit.

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Moreover, it can be shown that flame retardancy and chemical resistance are improved in formulations containing compatibilizers in comparison to those which do not contain compatibilizers.

Claims

1. A flexible, nonhalogen-containing polymer composition comprising a blend of
 - (1) ethylene vinyl acetate containing 30-90% by weight ethylene and 10-70% by weight vinyl acetate;
 - (2) very low density polyethylene having a specific gravity less than 0.920; and
 - (3) ethylene vinyl acetate carbon monoxide terpolymer containing 30-90% by weight ethylene, 10-70% by weight vinyl acetate and 1-20% by weight carbon monoxide.
 2. A blend according to claim 1 wherein component (1) comprises 5-65 % by weight of the blend, component (2) comprises 5-65 % by weight of the blend, and component (3) comprises 5-65 % by weight of the blend.
 3. A blend according to claim 1 wherein component (1) comprises 20-50% by weight of the blend, component (2) comprises 10-40% by weight of the blend and component (3) comprises 20-50% by weight of the blend.
 4. A blend according to claim 1 further comprising
 - (4) a compatibilizer blend comprising
 - (i) a polar olefinic polymer containing 15 to 60% by weight ethylene vinyl acetate; and
 - (ii) a non-polar olefinic polymer
- wherein one of components (4)(i) and (4)(ii) contains 0.01 to 10% by weight of glycidyl acrylate or methacrylate or a derivative thereof, and the other of components (4)(i) and (4)(ii) contains 0.01 to 10% by weight of a carboxylic acid or a derivative thereof.

5. A blend according to claim 4 wherein component (4) comprises 0.5-10% by weight of the blend.
- 5 6. A shaped article formed from a blend according to claim 1.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US95/11052

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C08F 255/02; C08L 23/02; C08G 67/02

US CL : 525/63, 74, 185, 190

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 525/63, 74, 185, 190

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

DERWENT (WORLD PATENT INDEX), APS

search terms: eva, vldpe, ldpe, carbon monoxide, ethylene vinyl acetate

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	US, A, 5,434,217 (SPELTHANN) 18 July 1995, columns 5-9.	1-6
X,P	US, A, 5,395,881 (SPELTHANN) 07 March 1995, columns 2-5.	1-6
Y	US, A, 5,089,556 (TABOR ET AL) 18 FEBRUARY 1992, COLUMNS 5-9.	1-6

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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